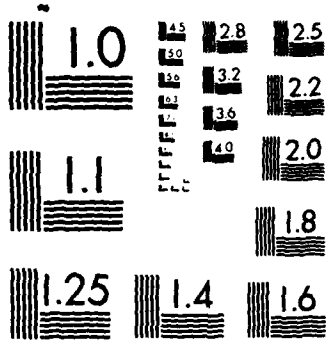
AD-A163 065 DISSOCIATIVE ELECTRON ATTACHMENT TO ROVIBRATIONALLY EXCITED MOLECULES(U) WAYNE STATE UNIV DETROIT MICH DEPT OF PHYSICS J M WADEHRA 30 SEP 85 AFOSR-TR-85-1133 1/1

UNCLASSIFIED AFOSR-84-0143 F/G 20/8 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

LASSIFIED

2

EPORT DOCUMENTATION PAGE

AD-A163 065

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release:
Distribution Unlimited

CLASSIFICATION/DOWNGRADING SCHEDULE

ORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 85-1133

E OF PERFORMING ORGANIZATION
e State University

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NP

RESS (City, State and ZIP Code)
ege of Liberal Arts
rtment of Physics & Astronomy
bit, MI 48202

7b. ADDRESS (City, State and ZIP Code)
Building 410
Bolling AFB DC 20332-6448

E OF FUNDING/SPONSORING ANIZATION

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR-84-0143

RESS (City, State and ZIP Code)

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61102F	2301/A	A7	

E (Include Security Classification)
SOCIATIVE ELECTRON ATTACHMENT TO ROVIBRATIONALLY EXCITED MOLECULES"

SONAL AUTHOR(S)
essor J.M. Wadehra

PE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
L	FROM 01 Aug 84 TO 30 Sep 85	30 Sep 85	10

PLEMENTARY NOTATION

COSATI CODES		
	GROUP	SUB. GR.

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

TRACT (Continue on reverse if necessary and identify by block number)

The aim of this project is to investigate
ependence of the cross sections for dissociative electron attachment to a molecule on
nitial rovibrational state of the molecule. An enhancement of the cross section
ts in the enhancement of the rate of production of negative ion beams. Preliminary
tigations reveal that for lithium dimers, Li(2), the peak attachment cross sections can
ase by almost an order of magnitude if the molecule is initially vibrationally excited
e v = 1 level. Excitation to higher vibrational levels would result in further
cement of the attachment rates. As part of present investigations, the cross sections
ibrational excitation of various molecules, using both resonant and nonresonant
nisms is calculated.

RIBUTION/AVAILABILITY OF ABSTRACT

SIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

ME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
Bruce L. Smith	202/767-4906	NP

RM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

AFOSR-TR- 1 1 0 9

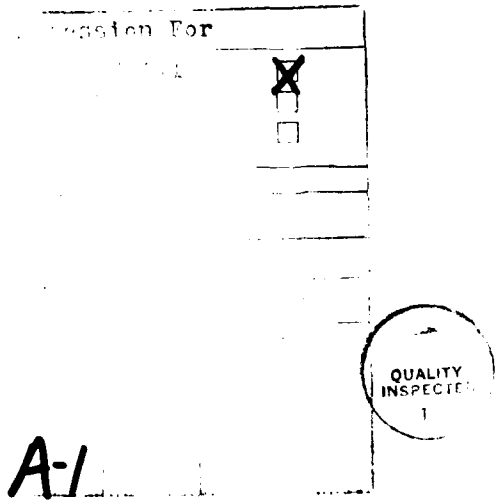
FIRST ANNUAL TECHNICAL REPORT

Project Title: Dissociative Electron Attachment to Rovibrationally Excited Molecules.

Grant Number: AFOSR-84-0143

Principal Investigator: Professor J. M. Wadehra
Department of Physics and Astronomy
Wayne State University

Date: September 30, 1985.



SUMMARY

The aim of this project is to investigate the dependence of the cross sections for dissociative electron attachment to a molecule on the initial rovibrational state of the molecule. An enhancement of the cross section results in the enhancement of the rate of production of negative ion beams. Preliminary investigations reveal that for lithium dimers, Li_2, the peak attachment cross sections can increase by almost an order of magnitude if the molecule is initially vibrationally excited to the v = 1 level. Excitation to higher vibrational levels would result in further enhancement of the attachment rates. As part of present investigations, the cross sections for vibrational excitation of various molecules, using both resonant and nonresonant mechanisms, are also calculated. In case of nonresonant mechanism, it is learnt that, for Li_2, vibrational levels up to v = 9 could be efficiently excited by first exciting the singlet A electronic state of the molecule and then allowing it to decay radiatively into various vibrational levels of the ground electronic state. For resonant mechanism, general models for vibrational excitation are developed in which the potential curves of the initial molecular state as well as the resonant anion state are approximated by simple harmonic oscillators. Closed form expressions along with convenient recursion relations for vibrational excitation amplitudes would allow rapid evaluation of cross sections for any inelastic or superelastic vibrational transition for various molecules.

The main objective of this research work (Grant Number AFOSR 84-0143) is to investigate the effect of temperature on the rate of production of negative ion beams via the process of dissociative electron attachment to diatomic molecules. Dissociative attachment to a molecule AB proceeds through the formation of an intermediate resonant state,

$$e + AB \rightarrow AB^- \rightarrow A + B^- \ .$$

The resonant state is also capable of autodetachment leaving behind a rovibrationally excited molecule,

$$AB^- \rightarrow AB(v,J) + e.$$

Raising of temperature essentially amounts to exciting the molecule to a higher rovibrational level. For certain diatomic molecules, notably H_2, it is observed that the rate of electron attachment is significantly enhanced if the molecule is initially rovibrationally excited. In the present investigations, the role played by the initial rovibrational excitation in enhancing the rate of electron attachment to other molecules like Li_2, CO, $HC\ell$, O_2 etc. is being understood. Also, as part of the investigations, the cross sections and rates for vibrational excitation of these molecules by both resonant and nonresonant processes are determined.

The following specific advances have been made during the first year of investigations:

a) The first molecule under investigation is the lithium dimer, Li_2. The electronic structure including the potential curves of both Li_2 and Li_2^- has been determined only recently. The similarity between Li_2 and H_2 (both are isoelectronic in the valence shell) and their corresponding anions suggests that theoretical approaches used successfully in the past for investigating the rates and cross sections for dissociative electron attachment and vibrational excitation of H_2 could be adapted for similar investigations of Li_2. In particular, local width resonant scattering theory is used for obtaining the

cross sections for dissociative attachment to Li_2, $e + Li_2 \rightarrow Li + Li^-$, as a function of the incident electron energy. Figure 1 shows the results of such a calculation. The structure seen in this figure is possibly an artifact of the limited range of internuclear separations over which the resonant nuclear wave function is extended. The factors by which the attachment cross sections for Li_2 are enhanced, on rovibrationally exciting the molecule initially, are summarized and compared with H_2 in the table below.

Initial vibrational level, v, the molecule is in.	Factor by which the peak attachment cross section is enhanced over that for v = 0.		
	Li_2	H_2 (Theory)	H_2 (Experiment)
1	7.4	32.5	30 ± 10
2	16.4	465	500 ± 175

The local width for the resonant state Li_2^- used in the present calculations is obtained by using the Fermi golden rule. The attachment cross sections are obtained only for low excitations of the molecule. For high excitations of the molecule it would be essential to use the nonlocal aspects of the resonant scattering theory. A complete determination of the matrix element, coupling the discrete resonant state with the continuum states, as a function of both the internuclear separation R and the incident electron energy E would suffice to carry out in the near future a detailed accurate nonlocal width calculation of attachment rates. Some preliminary results of calculations of cross sections for electron attachment to Li_2 were presented at the Fourteenth International Conference on the Physics of Electronic and Atomic Collisions in Palo Alto, California. It is anticipated that these results along with the results of a nonlocal width calculation for the cross sections and rates of attachment to Li_2 will be sent for publication in a refereed journal.

b) In order to understand the behavior of cross sections for excitation to various vibrational levels of Li_2 it is important to consider both the resonant and the nonresonant processes. The resonant vibrational excitation cross sections, of course, follow as a byproduct of the calculations of dissociative attachment since autodetachment of the resonant anion state competes with the dissociation process. As a possible nonresonant mechanism of vibrationally exciting the molecule, one could consider the following two step process. As first step, molecule Li_2 is excited from its ground $X\,^1\Sigma_g^+$ state to a higher singlet state either by electron impact or by photon pumping. Schematically,

$$e + Li_2\ (X\ ^1\Sigma_g^+,\ v_i) \rightarrow Li_2\ (A\ ^1\Sigma_u^+,\ B\ ^1\pi_u) + e$$

or $$Li_2\ (X\ ^1\Sigma_g^+,\ v_i) + h\nu \rightarrow Li_2\ (A\ ^1\Sigma_u,\ B\ ^1\pi_u).$$

In the second step, the excited molecule undergoes a rapid radiative decay to an excited vibrational level of the ground electronic state:

$$Li_2\ (A\ ^1\Sigma_u^+,\ B\ ^1\pi_u) \rightarrow Li_2\ (X\ ^1\Sigma_g^+,\ v_f) + h\nu\ .$$

Calculations of relative cross sections for excitation of higher vibrational levels of the ground electronic state of Li_2 by this nonresonant process indicate that in general the excitation occuring via the formation of $A\ ^1\Sigma_u^+$ electronic state is more efficient than via the formation of $B\ ^1\pi_u$ state. All the vibrational levels up to $v_f \sim 9$ are efficiently excited for both electron collisional excitation as well as the photon pumping of the A state. Details of the calculations have been published in the refereed journal, Chemical Physics Letters.

c) The process of resonant vibrational excitation of a molecule AB involves the formation of an autodetaching intermediate resonant anion state AB^-:

$$e + AB\ (v_n) \rightarrow AB^- \rightarrow AB\ (v_m) + e.$$

In order to obtain the cross sections for vibrational excitation using this mechanism, one needs to know the potential curves of AB and AB^- and the

resonance width Γ of AB^-. Under present investigation is a simple model in which the potential curves of AB and AB^- are replaced by those of simple harmonic oscillators with frequencies ω and ω^-, respectively. The two oscillators are displaced from one another by internuclear separation R_0. The reduced mass of the nuclei is μ. The energy dependent width Γ is assumed to be independent of the internuclear separation R. For convenience define

$$A = (\omega - \omega^-)/(\omega + \omega^-), \quad \omega_0 = 2\hbar/\mu R_0^2.$$

Then under the impact of an electron of mass M and energy $E = (\hbar k_i)^2/2M$, the molecule makes a transition from level with vibrational quantum number n to a level with vibrational quantum number m. Energy of the outgoing electron is obtained from the conservation of energy:

$$(\hbar k_f)^2/2M = (\hbar k_i)^2/2M + \hbar\omega(n + \tfrac{1}{2}) - \hbar\omega(m + \tfrac{1}{2}).$$

The amplitude for vibrational excitation under these circumstances can be written in a closed form expression,

$$A(n \to m;\ z) = -\frac{2\pi}{\sqrt{k_i k_f}} \frac{\Gamma}{\hbar\omega^-} \left(-\frac{A}{2}\right)^{\frac{n+m}{2}} \sqrt{\frac{1-A^2}{n!m!}} \exp\left(-\sqrt{\frac{(1-A^2)}{\omega_0^2}} \cdot \omega\omega^-\right)$$

$$\sum_{j=0}^{\min(n,m)} j!\ \binom{n}{j}\binom{m}{j}\left(-\frac{2(1-A^2)}{A}\right)^j$$

$$\int_0^1 dt\ t^{-(z+1)+j}\ \frac{(1-t^2)^{\frac{n+m}{2}-j}}{(1-A^2t^2)^{\frac{n+m+1}{2}}}\ \exp\left\{\frac{\omega}{\omega_0}\frac{(1-A^2)t}{1+At}\right\}\ H_{n-j}(f(t))H_{m-j}(f(t)),$$

where H_k is a Hermite polynomial of order k with argument

$$f(t) = \left[\frac{(1-A^2)\omega^-}{2A\omega_0}\ \frac{(t-1)(1-At)}{(t+1)(1+At)}\right]^{\frac{1}{2}}.$$

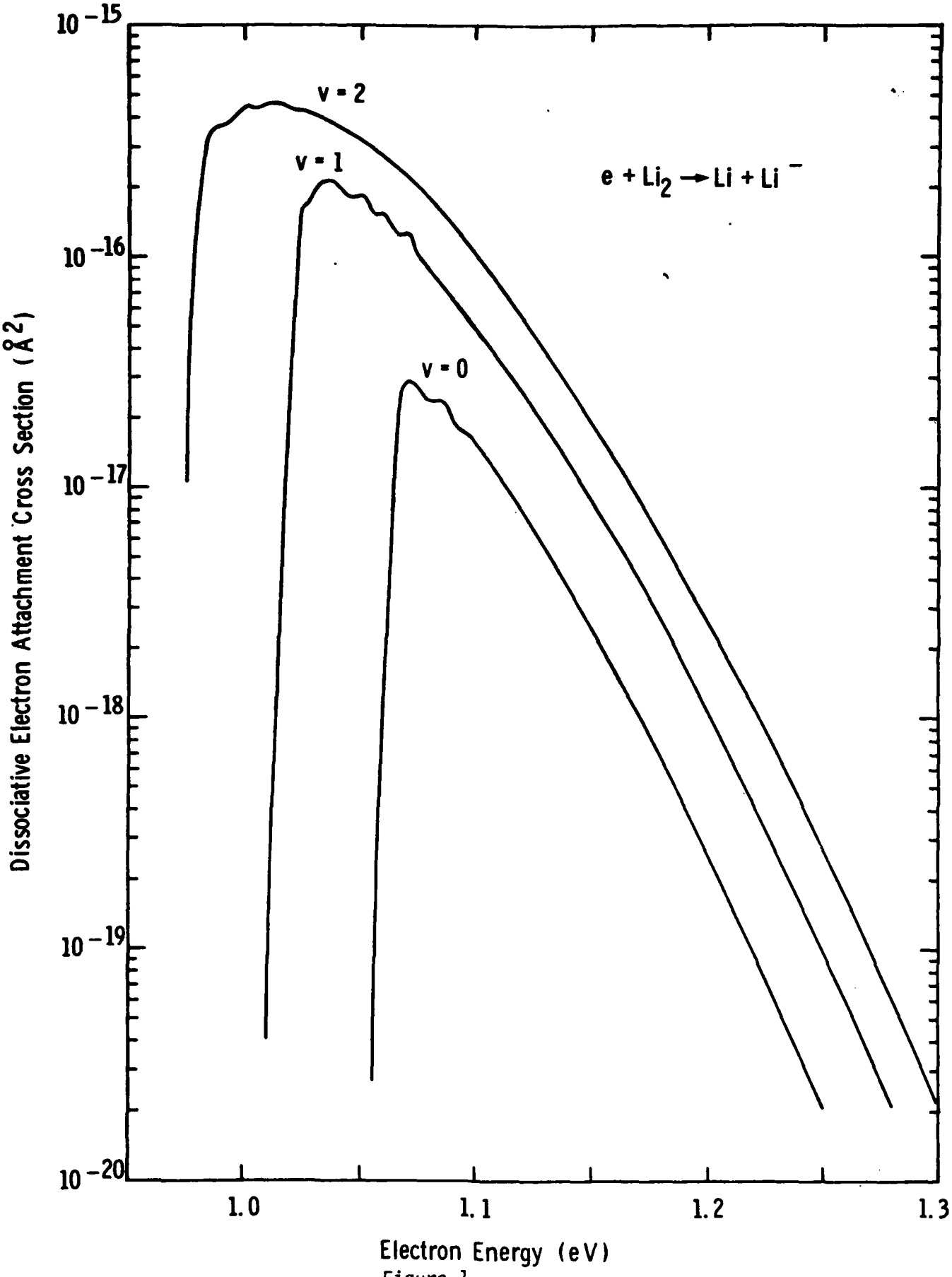

10^{-15}
10^{-16}
10^{-17}
10^{-18}
10^{-19}
10^{-20}
v = 2
v = 1
v = 0
$e + Li_2 \rightarrow Li + Li^-$
Dissociative Electron Attachment Cross Section ($Å^2$)
1.0
1.1
1.2
1.3
Electron Energy (eV)

Figure 1

THIRTY-EIGHTH ANNUAL GASEOUS ELECTRONICS CONFERENCE

15-18 October 1985
MONTEREY, CALIFORNIA

PLEASE TYPE NAME, ADDRESS & TELEPHONE NUMBER

Dr. J. M. Wadehra
Wayne State University
Department of Physics
Detroit, MI 48202
(313) 577-2740

AUTHORS PLEASE NOTE

Indicate topic(s) covered in the paper by selecting a letter and a digit from the attached list. If more than one, present in order of importance.

Letter	Digit
C	1

Indicate preferred mode of presentation.

- ☒ Poster
- ☐ Lecture
- ☐ Either

DO NOT WRITE IN THIS SPACE

Serial No. _____

Accepted: Yes _____ No _____

Session _____

Number _____

Date. Conf. _____

Vibrational Excitation of Diatomic Molecules (N_2, CO, Li_2) during Resonance Scattering of Electrons,*

J.M. WADEHRA and P.J. DRALLOS, Wayne State University--

A one dimensional integral expression is obtained for the cross section for resonant vibrational excitation of diatomic molecules. The potential energy curves for both the neutral molecule as well as the resonant state are approximated by one dimensional harmonic oscillators having arbitrary curvatures and equilibrium positions. Results of the computations are obtained for the molecules N_2 and CO, and are in good agreement with experiment. Results for resonant vibrational excitation cross sections for Li_2 are also presented.

*Work supported by AFOSR Grant 84-0143

Publications/Presentations

1. "Dissociative Attachment in Low Energy e + Li_2 Collisions", (with H. H. Michels) presented at the 37th Gaseous Electronics Conference, Boulder, Colorado, October 9-12, 1984.
2. "Dissociative Electron Attachment to Molecular Lithium", (with H. H. Michels) presented at the Fourteenth International Conference on the Physics of Electronic and Atomic Collisions, Palo Alto, California, July 24-30, 1985.
3. "Vibrational Excitation and Dissociative Attachment", a review article in Vibrational Excitation, Dissociation and Ionization of Diatomic Molecules, M. Capitelli, ed. (Springer-Verlag, 1985).
4. "Vibrational Excitation of Li_2 via electron or photon excitation of the A $^1\Sigma_u^+$ and B $^1\pi_u$ states", (with H. H. Michels) Chem. Phys. Lett. 114, 380 (1985).
5. "Vibrational Excitation of diatomic molecules during resonance scattering of electrons", (with P. J. Drallos) to be presented at the Thirty Eighth Gaseous Electronics Conference, Monterey, California, October 15-18, 1985.

z is a complex quantity containing the incident electron energy E:

$$z = (E + i\tfrac{1}{2}\Gamma/\hbar\omega^{-} - \tfrac{1}{2} + (n + \tfrac{1}{2})\omega/\omega^{-}.$$

Of special interest is the case $\omega = \omega^{-}$ which corresponds to simple harmonic oscillators of equal frequencies. In this case $A \to 0$ and the transition amplitude becomes

$$A(n \to m;\ z) = (-1)^{n+m+1} \frac{2\pi}{\sqrt{k_i k_f}} \frac{\Gamma}{\hbar\omega} \left(\frac{\omega}{\omega_o}\right)^{\frac{n+m}{2}} \frac{1}{\sqrt{n!m!}} \exp\left(-\frac{\omega}{\omega_o}\right)$$

$$\sum_{j=o}^{\min(n,m)} j! \binom{n}{j}\binom{m}{j}\left(\frac{\omega_o}{\omega}\right)^{j} \int_0^1 dt\ t^{-z-1+j}(1-t)^{n+m-2j} \exp\left(\frac{\omega t}{\omega_o}\right)$$

$$= \sum_{j=o}^{\min(n,m)} \frac{[n!m!(n+m-2j)!]^{\frac{1}{2}}}{j!(n-j)!(m-j)!} A(0 \to n+m-2j;\ z-j) \quad . \qquad [1]$$

This interesting relationship suggests that the amplitude for <u>any</u> transition, inelastic or superelastic, can be written as a linear combination of inelastic amplitudes alone. Furthermore the inelastic amplitudes satisfy the following recursion relation,

$$\sqrt{m+1}\ A(0 \to m+1) - \left(\sqrt{\frac{\omega}{\omega_o}} + \sqrt{\frac{\omega_o}{\omega}}\ (m-z)\right) A(0 \to m) + \sqrt{m}\ A(0 \to m-1) = 0 \ . \quad [2]$$

Thus the amplitude for any transition can be obtained, using Eqs. [1] and [2], in terms of $A(0 \to 0)$ and $A(0 \to 1)$ only. The principal investigator, along with a graduate research assistant Mr. P. Drallos, is obtaining the recursion relations, similar to [1] and [2] above, for the case of unequal frequencies of the two oscillators ($\omega \neq \omega^{-}$). These analytical results along with numerical values of vibrational excitation cross sections for various molecules will be presented at the Thirty Eighth Gaseous Electronics Conference, Monterey, California in October 1985.

END

FILMED

2-86

DTIC